

# Causes of Large Increases in Atmospheric Ammonia in the Last Decade across North America

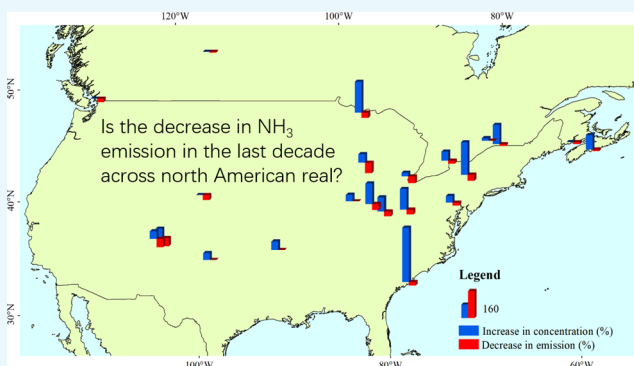
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## Supporting Information

**ABSTRACT:** Decadal trends of atmospheric ammonia ( $\text{NH}_3$ ) and their potential causes were explored through the analysis of monitored data collected at 15 sites in the United States and 7 sites in Canada. Large percentage increases in the annual average concentration of atmospheric  $\text{NH}_3$ , for example, >100% at 6 sites and 40–100% at 10 sites, were observed over the most recent 8–13 year period. In contrast, a decrease or a narrow variation in  $\text{NH}_3$  emissions was reported at the state or provincial level in both countries during the same period. Decreased emissions of  $\text{SO}_2$  and  $\text{NO}_x$  across North America in the past decade would have reduced the chemical loss of atmospheric  $\text{NH}_3$  to form particulate  $\text{NH}_4^+$ . Such a chemical mechanism was verified through regression analysis at about half of the monitored sites, where the increasing trends in atmospheric  $\text{NH}_3$  were partially explained by the reduced  $\text{NH}_4^+$ . Excluding the reduced contribution from this chemical loss to generate the adjusted annual  $\text{NH}_3$  concentration through two approaches, no decreasing trends can be obtained to align those in emissions at most sites, implying that other factors also contributed to the increase in the annual  $\text{NH}_3$  concentration. Correlation analysis results implied that enhanced drought conditions and increased ambient temperatures also likely contributed to the increasing trend in the annual  $\text{NH}_3$  concentration at some sites. The large percentage increases in the annual  $\text{NH}_3$  concentration cannot be fully explained by all the identified causes, leading to oppugning the reality of the decrease in  $\text{NH}_3$  emissions reported across North America in the recent decade.



## 1. INTRODUCTION

Atmospheric ammonia ( $\text{NH}_3$ ) plays an important role in nitrogen cycling and on ecosystem health.<sup>1,2</sup> Excess input of nitrogen to sensitive ecosystems can cause various negative impacts.<sup>3</sup> Being the most abundant alkaline gas in the air, atmospheric  $\text{NH}_3$  can neutralize acidic species to form secondary aerosols, which can experience long-range transport and affect regional air quality as well as climate.<sup>4–9</sup> A large amount of synthetic nitrogenous fertilizers used for agricultural activities consequently increases  $\text{NH}_3$  concentrations at various spatiotemporal scales worldwide.<sup>10–12</sup> For example,  $\text{NH}_3$  concentrations were nearly 1 order of magnitude higher during fertilization periods than that during other times in agricultural areas across southern Ontario.<sup>11</sup> Decadal scale increases in  $\text{NH}_3$  concentrations have also been identified for China, Europe, the United States, and other countries using satellite data.<sup>12</sup>

North America is one of the most intensive  $\text{NH}_3$  emission zones on earth.<sup>12,13</sup> The established anthropogenic  $\text{NH}_3$  emission inventories show that agricultural  $\text{NH}_3$  emissions exceed 80% of the total anthropogenic  $\text{NH}_3$  emissions therein.<sup>14,15</sup> No regulations have been promulgated to reduce

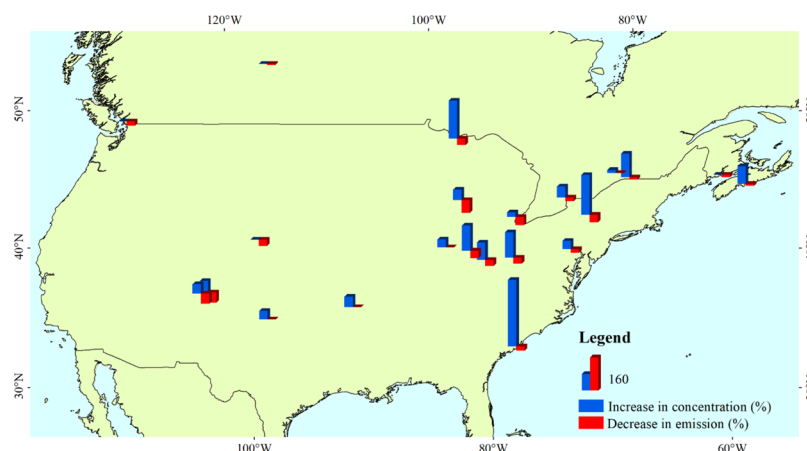
$\text{NH}_3$  emissions in North America, although decreased  $\text{NH}_3$  emissions have been reported in most provinces in Canada (<https://pollution-waste.canada.ca/air-emission-inventory>) and states in the United States (<https://www.epa.gov/air-emissions-inventories/air-emissions-sources>). On the other hand, increasing trends in  $\text{NH}_3$  concentrations have been identified from satellite observations and ground-level measurements.<sup>2,12,16</sup> The contrasting trends between  $\text{NH}_3$  emissions and concentrations have not been fully explained,<sup>12,17</sup> which hampers efforts to accurately assess nitrogen-related impacts and make proper emission control policies.<sup>2,18,19</sup>

The chemical mechanism that has reduced formation of particulate ammonium ( $\text{NH}_4^+$ ) because of emission reductions of  $\text{SO}_2$  and  $\text{NO}_x$  should theoretically reduce the chemical loss of atmospheric  $\text{NH}_3$  and has been argued as a major factor affecting the annual trend in atmospheric  $\text{NH}_3$ .<sup>12,16,17</sup> Climate anomalies may also affect the trend in atmospheric  $\text{NH}_3$  to

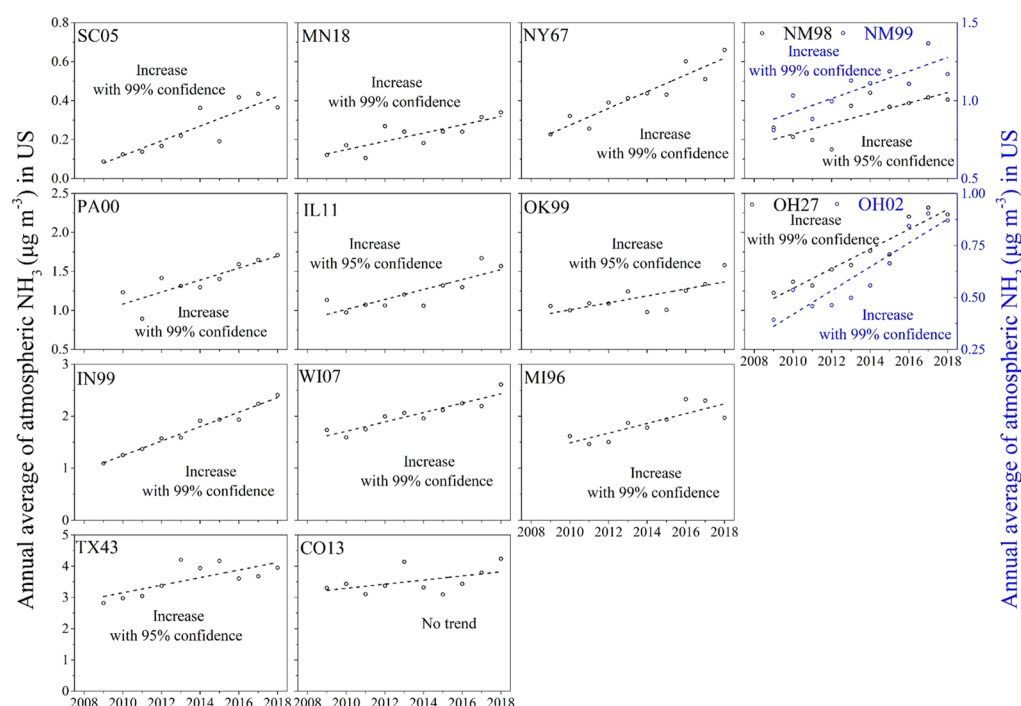
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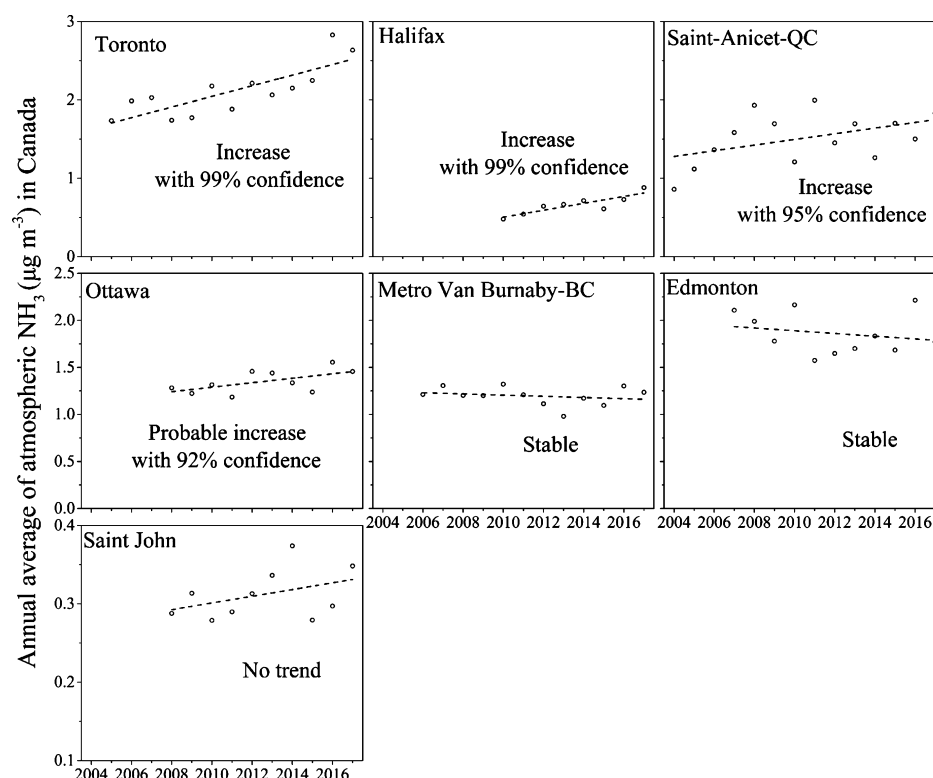
**Figure 1.** Geographical distributions of the percentage increase in annual  $\text{NH}_3$  concentrations at each sampling site and percentage decreases in the  $\text{NH}_3$  annual emissions in each corresponding state or province reported across North America (0 represents no decreasing or increasing trends, map is free domain).



**Figure 2.** Trends in the annual  $\text{NH}_3$  concentration observed at 15 sites in the United States (dashed line represents LR results).

some extent because the release of  $\text{NH}_3$  from agricultural activities not only depends on the amount of fertilizer applied but also depends on weather conditions during and after the fertilization period.<sup>10,20</sup> For example, the largest  $\text{NH}_3$  emissions from fertilizer applications and from livestock sectors were reported in May across southern Ontario.<sup>21</sup> However, the maximum value of atmospheric  $\text{NH}_3$  was reportedly observed in July at various agricultural and remote sites therein using passive samplers.<sup>11</sup> Atmospheric  $\text{NH}_3$  has been reported to be vulnerable to climate warming, for example,  $\text{NH}_3$  volatilization potential from soil/vegetation systems nearly doubles with every 5 °C increase in air temperature.<sup>20,22</sup> In the last decade, from 2009 to 2018, 8 years were among the 10 hottest global years on record, with 2015–2018 being ranked as the top 4 hottest years; thus, the response of atmospheric  $\text{NH}_3$  concentrations to climate anomalies is worth further investigation.

The present study aims to identify long-term trends and their causes in atmospheric  $\text{NH}_3$  at the available monitoring sites across Canada and the United States (Tables S1 and S2). To achieve these goals, total  $\text{NH}_3$  emissions as well as  $\text{NH}_3$  emissions from transportation and wildfire sectors at Canadian provincial and US state levels were both analyzed along with variations in annual  $\text{NH}_3$  concentrations. Correlations between the annual average concentrations of  $\text{NH}_3$  and  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$  were also analyzed to elucidate the influence of chemical conversion of  $\text{NH}_3$  to  $\text{NH}_4^+$  on  $\text{NH}_3$  trends. Building on the analysis results, the annual  $\text{NH}_3$  concentrations were adjusted by excluding the reduced loss caused by chemical conversion of  $\text{NH}_3$  to  $\text{NH}_4^+$  through two approaches and were reexamined for the trends. Finally, the impact of weather conditions, including the ambient temperature and Palmer drought index (PDI), on  $\text{NH}_3$  trends was explored. Knowledge gained from this study reveals the need to verify the reported  $\text{NH}_3$



**Figure 3.** Trends in the annual  $\text{NH}_3$  concentration observed at seven sites in Canada (dashed line represents LR results).

emissions in both countries and for continued monitoring over long time scales and at more locations.

## 2. RESULTS AND DISCUSSION

### 2.1. Trends in the Annual Average Mass Concentration of Atmospheric $\text{NH}_3$ across the United States.

An increasing trend from 2009/2010 to 2018 was identified in the annual average mass concentration of atmospheric  $\text{NH}_3$  at 14 out of the 15 sites in the United States from Mann–Kendall (M–K) and linear regression (LR) analyses at a 95% confidence level (Figures 1 and 2). No trend was found at site CO13 (a site in Colorado). The total percentage increases during the study period exceeded 100% at five sites, ranged from 40–100% at eight sites, and was only ~20% at site MI96 in Michigan (Figure 1). Larger percentage increases were generally associated with sites with lower annual  $\text{NH}_3$  concentrations (Figure 2). For example, five sites (SC05, MN18, NY97, OH02, and NM98) had annual  $\text{NH}_3$  concentrations lower than  $1 \mu\text{g m}^{-3}$  (a critical level of atmospheric  $\text{NH}_3$  for sensitive ecosystems, as reported by Cape et al., 2009<sup>23</sup>). Among these, the largest percentage increase of >300% was observed at SC05, a remote site in Cape Romain National Wildlife Refuge, South Carolina, with the annual  $\text{NH}_3$  concentration increasing from  $0.09 \mu\text{g m}^{-3}$  in 2009 to  $0.4 \mu\text{g m}^{-3}$  in 2018. An ~200% increase was observed at MN18 in Minnesota and NY67 in New York, followed by an ~120% increase at OH02 in Ohio and only an ~60% increase at NM98 in New Mexico.

The annual  $\text{NH}_3$  concentrations were generally higher than  $1 \mu\text{g m}^{-3}$  at the other nine American sites (IN99, MI96, TX43, NM99, PA00, IL11, OK99, WI07, and OH27) that were identified to have increasing trends. The percentage increases in annual  $\text{NH}_3$  concentrations were less than 100% at all of these sites except IN99, ~120%. A rural site with intensive

agricultural activities (TX43 in Texas) had annual  $\text{NH}_3$  concentrations generally exceeding  $3 \mu\text{g m}^{-3}$ . The percentage increase at TX43 was approximately 40% from 2009 to 2018, but there were two distinctive periods when the annual  $\text{NH}_3$  concentrations jumped from  $3.1 \pm 0.2 \mu\text{g m}^{-3}$  (the mean  $\pm$  standard deviation) in 2009–2012 to  $3.9 \pm 0.3 \mu\text{g m}^{-3}$  in 2013–2018. However, within each of these two periods, there were only narrow annual variations, and there were no distinctive seasonal trends. The inflection point occurred in 2011–2013 when  $\text{NH}_3$  concentrations showed a clear oscillating increase, starting from a lower value of  $1.0 \mu\text{g m}^{-3}$  in October 2011 to a higher value of  $5.4 \mu\text{g m}^{-3}$  in November 2012 to January 2013 (Figure S1a). These phenomena suggest possible increases in anthropogenic  $\text{NH}_3$  emissions during October 2011 to January 2013, and the emissions remained at high levels afterward. Similar to what happened at TX43, large increases in annual  $\text{NH}_3$  concentrations at most of the American sites occurred after 2011–2012. However, the large increases in annual  $\text{NH}_3$  concentrations apparently continued from 2011–2012 to 2018 at these sites rather than the narrow oscillation observed at TX43 in 2013–2018.

For the site that had no clear trend (CO13), the annual  $\text{NH}_3$  concentrations oscillated around  $3.5 \pm 0.4 \mu\text{g m}^{-3}$  during 2009–2018 but narrowly decreased to around  $3.4 \pm 0.2 \mu\text{g m}^{-3}$  if the two highest values of  $4.1$ – $4.2 \mu\text{g m}^{-3}$  in 2013 and 2018 were excluded. These two highest annual values were likely related to the effects of climate anomalies because the reported  $\text{NH}_3$  emissions in CO decreased by approximately 30% from 2009 to 2017 (Figure 1). Li et al. also reported a stable annual mean value of  $\text{NH}_3$  concentrations in summer time through 2010–2015 in the northeastern plains of Colorado.<sup>24</sup>

### 2.2. Trends in the Annual Average Mass Concentration of Atmospheric $\text{NH}_3$ across Canada.

An increasing

trend in the annual average mass concentration of atmospheric  $\text{NH}_3$  was identified at three sites, that is, an urban site in Halifax, Nova Scotia, from 2010 to 2017, an urban site in Toronto, Ontario, from 2005 to 2017, and a rural agricultural site in Saint-Anicet, Québec, from 2006 to 2017 (Figure 3); these were identified from M–K and LR analyses at 95% confidence levels. A probable increasing trend was also resolved at an urban site in downtown Ottawa from 2008 to 2017 from the M–K method with a 92% confidence level. A stable trend at two urban sites (Metro Van Burnaby, British Columbia, and Edmonton, Alberta) and no trend at one urban site (Saint John, New Brunswick) in the last decade were also resolved from the M–K method. It is interesting that an obvious increase in annual  $\text{NH}_3$  concentrations occurred in Toronto after 2011, which was similar to what happened at most of the American sites. If the annual  $\text{NH}_3$  concentration only during the period from 2005 to 2011 in Toronto was considered alone, no trend was resolved by the M–K method.

The percentage increase was  $\sim 110\%$  from 2004 to 2017 at the rural site in Québec,  $\sim 80\%$  from 2010 to 2017 in downtown Halifax, and  $\sim 50\%$  from 2005 to 2017 in downtown Toronto. At the rural site in Québec, the annual  $\text{NH}_3$  concentration linearly increased from  $0.9 \mu\text{g m}^{-3}$  in 2004 to  $1.9 \mu\text{g m}^{-3}$  in 2008 and then largely oscillated around  $1.9 \pm 0.3 \mu\text{g m}^{-3}$  during 2008–2017. The annual  $\text{NH}_3$  concentration increased from  $0.5 \mu\text{g m}^{-3}$  in 2010 to  $0.9 \mu\text{g m}^{-3}$  in 2017 in Halifax and from  $1.7 \mu\text{g m}^{-3}$  in 2005 to  $2.6 \mu\text{g m}^{-3}$  in 2017 in Toronto. Annual  $\text{NH}_3$  concentrations narrowly varied around  $1.3 \pm 0.1 \mu\text{g m}^{-3}$  from 2008 to 2017 in downtown Ottawa,  $1.2 \pm 0.1 \mu\text{g m}^{-3}$  from 2006 to 2017 in Metro Van Burnaby, and  $0.3 \pm 0.03 \mu\text{g m}^{-3}$  from 2008 to 2017 in Saint John, but they varied in a larger range of  $1.6\text{--}2.2 \mu\text{g m}^{-3}$  in Edmonton. Unlike the findings at sites with low annual  $\text{NH}_3$  concentrations in the United States, no large percentage increase in the annual  $\text{NH}_3$  concentration occurred in Saint John.

**2.3. Comparison of the Trends in Atmospheric  $\text{NH}_3$  and the Reported  $\text{NH}_3$  Emissions.** The discussions above showed that when combining the U.S. and Canadian sites, 6 out of the 22 studied sites had a percentage increase in annual  $\text{NH}_3$  concentrations exceeding 100% and 10 sites had an increase of 40–100% in the last 8–13 years. To explore the dominant factors causing these increases, the  $\text{NH}_3$  emission trends reported in both countries were first examined.

The reported state-level total  $\text{NH}_3$  emissions decreased by 30–60% in the states of IN, MI, MN, NM, NY, and WI, and they decreased by 20–30% in the states of CO, OH, PA, and SC from 2009 to 2017 (Figure 1). Apparently, the decreasing emission trends cannot explain the large increasing trends in atmospheric  $\text{NH}_3$  at the sites located in these states. The state-level total  $\text{NH}_3$  emissions narrowly oscillated, for example, with the standard deviation over the mean of the total annual  $\text{NH}_3$  emissions being within 2% in IL, OK, and TX from 2009 to 2017. Again, such emission trends were not consistent with the 40–50% increase in the annual  $\text{NH}_3$  concentrations measured at IL11, TX 43, and OK99.

$\text{NH}_3$  emissions from transportation have been considered an important source of atmospheric  $\text{NH}_3$  in urban environments, as reviewed by Behera et al. (2013),<sup>10</sup> although this has been argued by others.<sup>25,26</sup> Annual  $\text{NH}_3$  emissions from transportation were reported to have decreased by 10–40% from 2009 to 2017 in the above-mentioned 13 states containing sites with atmospheric  $\text{NH}_3$  measurements. The decreasing emission trends cannot explain the increasing trends in

atmospheric  $\text{NH}_3$  at several urban sites (MI96, OH27, and NM99).

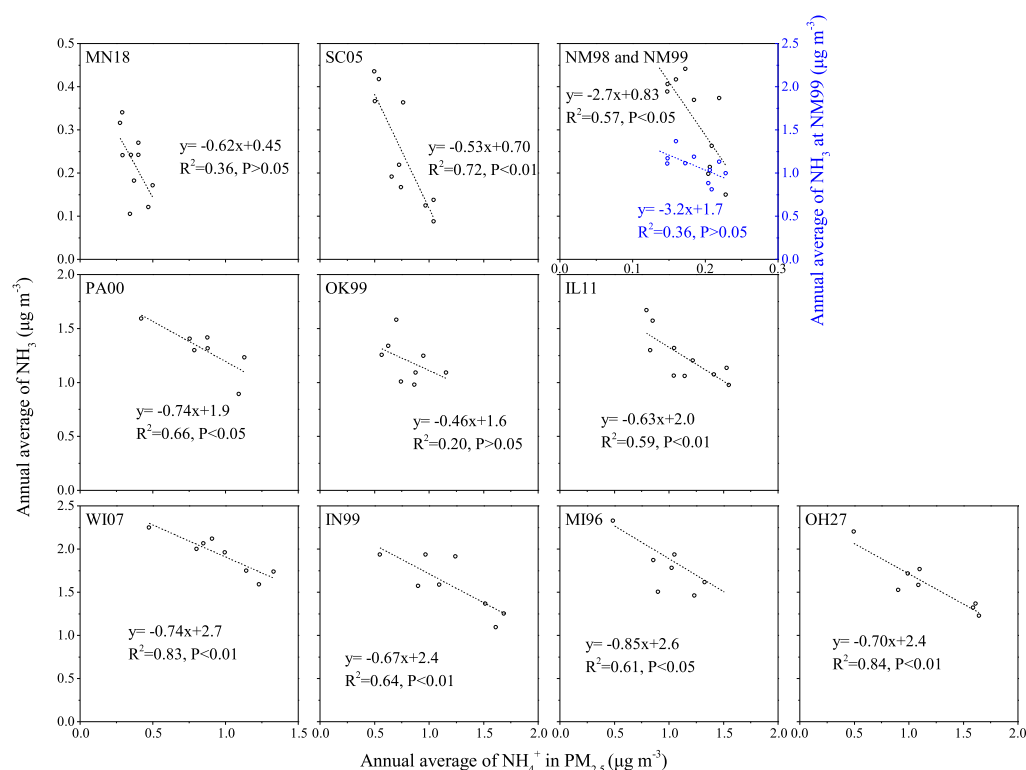
$\text{NH}_3$  emissions from wildfires are an important source of atmospheric  $\text{NH}_3$  in remote and rural environments.<sup>27</sup> Emissions from this source were expected to be higher in drought years than in ordinary years, such as in 2011 when one of the worst droughts occurred in NM, TX, and CO (Figure S2). The reported annual  $\text{NH}_3$  emissions from the wildfires in NY, OH, and PA increased greatly from 2010/2011 to 2014 and then remained nearly constant during 2014–2017. However, those in MN showed a large decrease from 2011 to 2014 and then remained low during 2014–2017. The patterns of the annual  $\text{NH}_3$  emissions from wildfires in these states were clearly inconsistent with the increasing trends in atmospheric  $\text{NH}_3$  monitored at respective remote/rural sites.

Similar to the case in the United States, provincial level total  $\text{NH}_3$  emissions reportedly decreased in eastern Canada, for example, an approximately 10% decrease from 2009 to 2017 in Nova Scotia, 20% from 2004 to 2017 in Ontario, and 10% from 2003 to 2017 in Québec (Figure 1).  $\text{NH}_3$  emissions from transportation had also reportedly decreased in the last decade in Canada, for example, an approximately 10% decrease in Nova Scotia from 2009 to 2017 and 40% decreases from 2004 to 2017 in Ontario and from 2003 to 2017 in Québec (figure not shown). The decreasing trends in  $\text{NH}_3$  emissions from transportation were clearly unable to explain the increasing or probable increasing trends in atmospheric  $\text{NH}_3$  at several urban sites (Halifax, Toronto, and Ottawa) in Canada. The large oscillation in annual  $\text{NH}_3$  around  $1.9 \pm 0.3 \mu\text{g m}^{-3}$  during 2008–2017 at the agricultural site in Québec was likely caused by perturbations in  $\text{NH}_3$  emissions regulated by weather conditions, as discussed below. However, drivers of the linear increase in the annual  $\text{NH}_3$  concentration from  $0.9 \mu\text{g m}^{-3}$  in 2004 to  $1.9 \mu\text{g m}^{-3}$  in 2008 at the same site have not been identified.

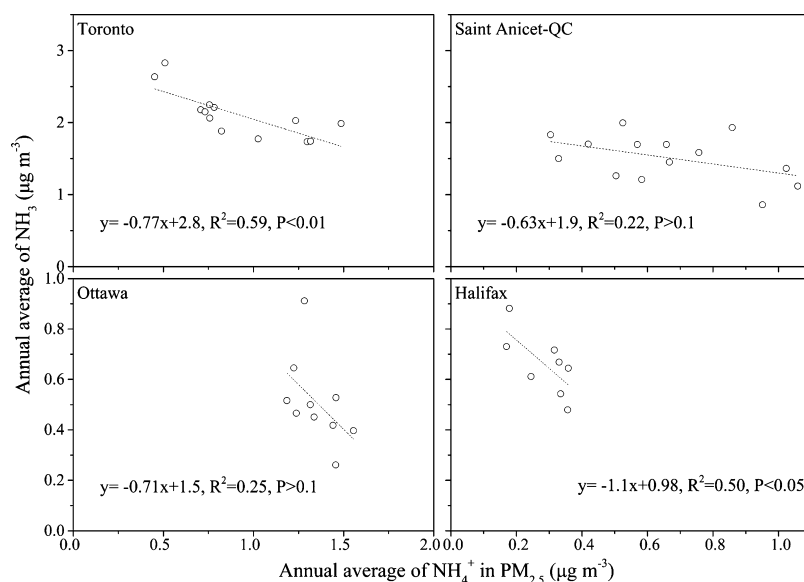
**2.4. Impact of  $\text{NH}_4^+$  Chemistry on the Increased Annual  $\text{NH}_3$  Concentrations.** **2.4.1. Increase in Atmospheric  $\text{NH}_3$  Related to Decreasing  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$ .** Decreases in emissions of  $\text{SO}_2$  and  $\text{NO}_x$  followed by reduced chemical conversion of  $\text{NH}_3$  to ammonium salts in atmospheric particles, have been widely debated as one of the major mechanisms causing the differing trends between atmospheric  $\text{NH}_3$  and  $\text{NH}_3$  emissions.<sup>12,17,28–32</sup> If this mechanism is the dominant factor controlling the  $\text{NH}_3$  trend, then any increased annual  $\text{NH}_3$  concentration should be reflected in the reduced annual  $\text{NH}_4^+$  concentration. Correlation analyses between the annual  $\text{NH}_3$  and  $\text{NH}_4^+$  concentrations were thus conducted below at the studied sites in the United States and Canada to reveal the extent that this chemical process contributed to the increased annual  $\text{NH}_3$  concentrations.

In the United States, no  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$  data were available at 6 out of the 15 sites (TX43, OH02, NY67, CO13, NM98, and NM99). The annual  $\text{NH}_4^+$  appeared to be highly homogeneous at a regional scale in the state of NM (Figure S3a). Thus,  $\text{NH}_4^+$  data at the nearby sites were used for NM98 and NM99. Correlation analyses between annual concentrations of  $\text{NH}_4^+$  and  $\text{NH}_3$  were thus conducted at 11 sites. These sites were grouped into three categories based on the obtained determination coefficients and slopes from the regression. In category 1, moderately good correlations ( $R^2 = 0.59\text{--}0.84$ ,  $P < 0.05$ ) between annual concentrations of  $\text{NH}_4^+$  and  $\text{NH}_3$  were indeed obtained at seven sites (SC05, PA00, IL11, WI07, IN99, MI96, and OH27) with the regression





**Figure 4.** Correlations between atmospheric  $\text{NH}_3$  and  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$  at 11 sites in the United States (dashed line represents LR results).



**Figure 5.** Correlations between atmospheric  $\text{NH}_3$  and  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$  at four sites in Canada (dashed line represents LR results).

slopes being close to  $-1.0$  ( $-0.5$  to  $-0.7$ , Figure 4). In this case, it can be safely assumed that the reduced chemical loss of atmospheric  $\text{NH}_3$  was likely a major contributor to the increased annual  $\text{NH}_3$  concentration. Slopes shallower than  $-1.0$  ones in these regressions were likely due to the longer residence time of  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$  compared to that of  $\text{NH}_3$  in the ambient air through atmospheric removal processes. In category 2 (NM98), the correlation was significant with  $P < 0.05$ , but the slope ( $-2.7$ ) was much steeper than  $-1.0$ , implying that the reduced chemical loss of atmospheric  $\text{NH}_3$  may be a minor contributor to the increased annual  $\text{NH}_3$  concentration. In category 3 (NM99, MN18, and OK99), no

significant correlations can be obtained, implying that other factors may overwhelm the reduced chemical loss of atmospheric  $\text{NH}_3$  in contributing to the increased annual  $\text{NH}_3$  concentration.

In Canada, moderately good correlations ( $R^2 = 0.50$ – $0.59$ ,  $P < 0.05$ ) between the annual concentrations of  $\text{NH}_4^+$  and  $\text{NH}_3$  were also obtained in Toronto and Halifax, with the regression slopes being  $-0.77$  to  $-1.1$  (Figure 5), suggesting that the reduced chemical loss of atmospheric  $\text{NH}_3$  was likely a major contributor to the increased annual  $\text{NH}_3$  concentration. No significant correlation existed in Saint-Anicet and Ottawa with  $P > 0.1$  (Figure 5), implying that other factors overwhelmed

the reduced chemical loss of atmospheric  $\text{NH}_3$  in contributing to the increased annual  $\text{NH}_3$  concentration. The same can be said at the other three Canadian sites with  $R^2 < 0.1$  and  $P > 0.05$  between the annual concentrations of  $\text{NH}_4^+$  and  $\text{NH}_3$  (figure not shown).

**2.4.2. Trends in Atmospheric  $\text{NH}_3$  with Reduced Chemical Loss Being Deducted.** To explore to what extent the reduced chemical losses contributed to the increased annual  $\text{NH}_3$  concentrations, the trends in the adjusted annual  $\text{NH}_3$  concentrations were reexamined after deducting the portions caused by the reduced chemical losses at several American sites. Two slightly different approaches were used herein. In the first approach, the 1:1 ratio was used to estimate the maximum potential concentration increase in atmospheric  $\text{NH}_3$  caused by the decreased  $\text{NH}_4^+$  formation. This approach is theoretically equivalent to extracting the trend in concentrations of annual  $\text{NH}_3$  plus annual  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$ , by assuming spatial homogeneity of annual  $\text{NH}_4^+$  over a regional scale.<sup>33</sup> For example, taking 2009 as the base year for site OH27, any net decrease in the annual  $\text{NH}_4^+$  concentration in future years relative to that in 2009 was assumed to increase the annual  $\text{NH}_3$  concentration equivalently. Such an approach should represent the maximum potential contribution from the reduced chemical loss to the increased annual  $\text{NH}_3$  concentration, as explained above for the results presented in Figure 4. Using this approach, the adjusted annual  $\text{NH}_3$  concentration in each year was then estimated as the original annual value minus the reduced chemical loss. The adjusted annual  $\text{NH}_3$  concentrations at OH27 showed a stable trend as resolved from the M–K method (Figure 6), in contrast to the trend of the reported  $\text{NH}_3$  emissions, which decreased by approximately 30% in OH. At the other 10 sites, the adjusted

annual  $\text{NH}_3$  concentrations showed stable trends at MN18, PA00, WI07, OK99, and MI96, no trend at NM98 and IN99, an increasing trend at NM99, and a likely decreasing trend at IL11 (figure not shown). Most of the adjusted annual  $\text{NH}_3$  concentrations at SC05 had negative values (Figure S4a), suggesting that this approach indeed overestimated the contribution of the reduced chemical loss to the increased  $\text{NH}_3$  concentration.

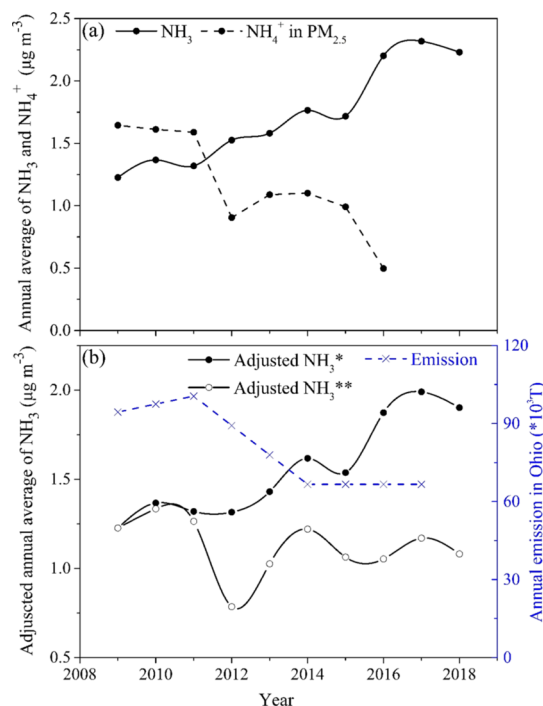
Thus, the second approach was designed to estimate the contribution of the reduced chemical loss to the increased  $\text{NH}_3$  concentration more accurately than the first approach does. In this approach, the cumulative effect of chemical loss was considered based on the available data, as detailed below. Taking site OH27 as the first example, the annual  $\text{NH}_4^+$  concentration at a nearby site (ID: 390610040, Table S3) a few kilometers away from OH27 experienced a two-phase decrease during the period of 2009–2016, that is,  $1.6 \pm 0.03 \mu\text{g m}^{-3}$  in 2009–2011,  $1.0 \pm 0.09 \mu\text{g m}^{-3}$  in 2012–2015, and  $0.5 \mu\text{g m}^{-3}$  in 2016 (Figure 6a). The two-phase decreases were also clearly observed at another site (ID: QUCI1, Table S3) situated in the same state (Ohio) but several hundred kilometers away from OH27, that is,  $1.4 \pm 0.05 \mu\text{g m}^{-3}$  in 2009–2011,  $1.1 \pm 0.04 \mu\text{g m}^{-3}$  in 2012–2015, and  $0.7 \pm 0.01 \mu\text{g m}^{-3}$  in 2016–2018 (Figure S3c). Thus, it can be assumed that the two-phase decreases in the annual  $\text{NH}_4^+$  concentration occurred on a regional scale covering site OH27. Using 2011 and 2012 as base years, the increase in  $\text{NH}_3$  in 2012 against 2011 was assumed to be completely caused by the reduced chemical loss, which apparently represents the upper limit estimation. The increased  $\text{NH}_3$  in future years (expressed as  $\Delta[\text{NH}_3]_x$  with  $x$  being the year of 2013, 2014, and so on) that can be attributed to the reduced chemical loss can then be estimated as

$$\Delta[\text{NH}_3]_x = ([\text{NH}_3]_{2012} - [\text{NH}_3]_{2011}) \times ([\text{NH}_4^+]_{2011} - [\text{NH}_4^+]_x) / ([\text{NH}_4^+]_{2011} - [\text{NH}_4^+]_{2012})$$

The  $\text{NH}_3$  concentrations at OH27 and the  $\text{NH}_4^+$  concentrations at site 390610040 were applied to the above equation.

Based on the consistent trend in annual  $\text{NH}_4^+$  concentrations from 2009 to 2016 at sites 390610040 and QUCI1 and the almost constant annual  $\text{NH}_4^+$  concentrations at QUCI1 during 2016–2018, it can be reasonably assumed that the chemical losses of atmospheric  $\text{NH}_3$  at OH27 in 2017 and 2018 were the same as that in 2016. The adjusted annual  $\text{NH}_3$  concentrations at OH27 after deducting  $\Delta[\text{NH}_3]_x$  are shown in Figure 6b. M–K and LR analysis results showed an increasing trend at a 99% confidence level, with an approximately 60% increase overall from 2009 to 2018. This approach is theoretically equivalent to extracting the trend in concentrations of annual  $\text{NH}_3$  plus  $\gamma^*$  annual  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$ , where  $\gamma$  is a coefficient between 0 and 1 and reflects the cumulative effect of chemical loss due to different deposition rates of atmospheric  $\text{NH}_3$  and particulate  $\text{NH}_4^+$ .

In the same state, there is another site (OH02) with monitored atmospheric  $\text{NH}_3$  data but without nearby  $\text{NH}_4^+$  data. Based on our previous findings, it still can be reasonably assumed that the values of  $([\text{NH}_3]_{2012} - [\text{NH}_3]_{2011})$  and  $([\text{NH}_3]_{2016} - [\text{NH}_3]_{2015})$  were completely due to the reduced chemical loss. The reduced chemical loss in each year of



**Figure 6.** (a) Annual averages of atmospheric  $\text{NH}_3$  at OH27 and  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$  at 390610040 in Ohio. (b) Adjusted annual averages of atmospheric  $\text{NH}_3$  at OH27 and  $\text{NH}_3$  emissions in Ohio. \* and \*\* indicate the adjusted annual averages based on approaches 2 and 1, respectively.

2012–2015 was assumed to be equal to  $([\text{NH}_3]_{2012} - [\text{NH}_3]_{2011})$ , while the reduced chemical loss in each year of 2016–2018 was assumed to be equal to the sum of  $([\text{NH}_3]_{2012} - [\text{NH}_3]_{2011})$  and  $([\text{NH}_3]_{2016} - [\text{NH}_3]_{2015})$ . The adjusted annual  $\text{NH}_3$  concentrations also exhibited an increasing trend with an approximately 80% overall increase from 2009 to 2018 (Figure S4b). The trends in the adjusted  $\text{NH}_3$  concentrations at both OH27 and OH02 implied a 60–80% increase in  $\text{NH}_3$  emissions in Ohio during 2009–2018, as opposed to the officially reported 30% decreases. Underestimation in the  $\text{NH}_3$  emissions was a common phenomenon globally.<sup>13</sup>

Using the second approach, increasing trends were also identified in the adjusted annual  $\text{NH}_3$  concentrations at IN99 and SC05, with the former site having an approximate 90% increase and the latter site having an  $\sim 260\%$  increase from 2009 to 2018 at a  $\geq 95\%$  confidence level (Figure S4b). Again, these percentage increases in  $\text{NH}_3$  concentrations were inconsistent with the reported 20–40% decreases in  $\text{NH}_3$  emissions in the respective U.S. states containing the considered sites. Note that the second approach cannot be applied to sites with larger annual  $\text{NH}_3$  concentrations in 2011 than those in 2012 or at sites with no distinctive two-phase decreases in annual  $\text{NH}_4^+$  concentrations.

**2.5. Increases in the Annual  $\text{NH}_3$  Concentration Related to Weather Conditions.** Because of a lack of soil and vegetation surface temperature data, ambient temperature is used alternatively for the analysis. The increase in ambient temperature would theoretically increase  $\text{NH}_3$  emissions from the soil and vegetation,<sup>24,25,34</sup> especially in the top four hottest years on record. When the annual  $\text{NH}_3$  concentration was correlated with the annual ambient temperature (Figure 7), a significant correlation was obtained only at OH02 ( $R^2 = 0.57$ ,  $P < 0.05$ ), OH27 ( $R^2 = 0.45$ ,  $P < 0.05$ ), and SC05 ( $R^2 = 0.57$ ,  $P$

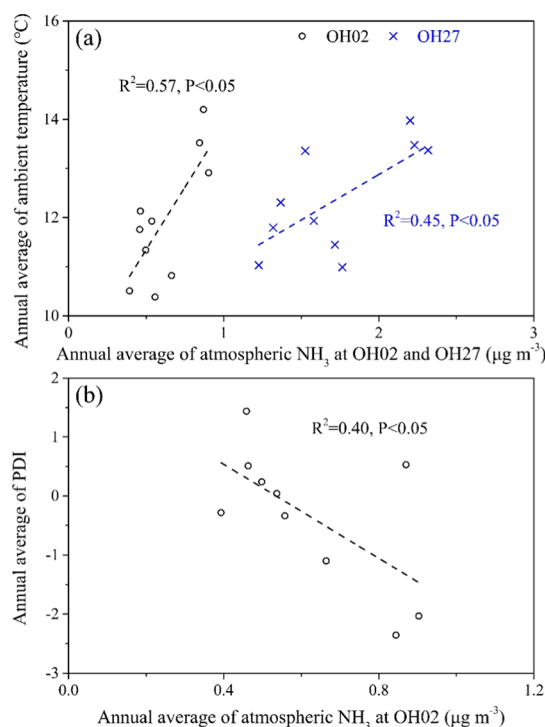
$< 0.05$ ; figure not shown). No correlation was found at the other sites, likely because other factors combined were dominant over the surface temperature in regulating ambient  $\text{NH}_3$ , including emissions from soil and vegetation.<sup>12,24,25,35</sup> A good exponential correlation between the atmospheric  $\text{NH}_3$  and ambient temperature (roughly representing the surface temperature with a few hour delay) may only exist in short time periods when other factors are weak, as reported in Hu et al. (2014)<sup>25</sup> and Teng et al. (2017).<sup>26</sup> The ambient temperature not only affects  $\text{NH}_3$  emissions but also affects the gas–aerosol partitioning of  $\text{NH}_3/\text{NH}_4^+$ .<sup>36,37</sup>

Recently, Warner et al. (2017) proposed that droughts led to increases in the annual  $\text{NH}_3$  concentration on the basis of satellite  $\text{NH}_3$  data and the ground-level drought index.<sup>12</sup> However, Teng et al. (2017) reported a large drop in concentrations of atmospheric  $\text{NH}_3$  during several dry days with water vapor below 3000 ppm and a positive correlation between  $\text{NH}_3$  concentrations and water vapor during many short time periods—from several hours to days.<sup>26</sup> In a laboratory experiment, the release of reactive nitrogen gases decreased to a negligible level when the soil was dried.<sup>38</sup> One explanation of the controversy between the above-mentioned studies is the different time scales focused in different studies. To explain the annual trend on a decadal scale, it is better to compare the annual  $\text{NH}_3$  concentration with annual drought data, such as that from PDI.

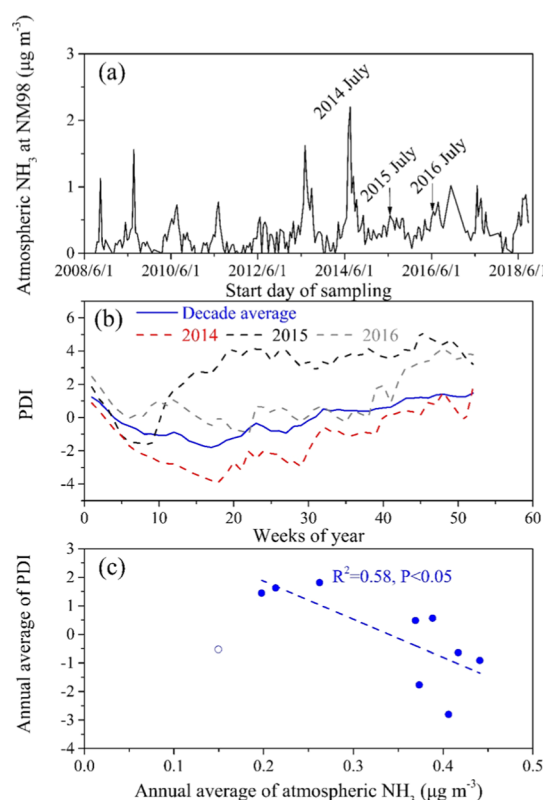
PDI has been widely used to quantify drought severity in the United States (Table S4). Drought usually occurs regionally, and it can be reasonably assumed that PDI at one site represents the regional drought extent. A significant negative correlation between the annual  $\text{NH}_3$  and PDI was obtained at OH02 ( $R^2 = 0.40$  or  $0.78$  with one outlier in 2018 being excluded; Figure 7b) and at NM98 if the outlier in 2012 was excluded ( $R^2 = 0.58$ ; Figure 8c). Thus, the influence of droughts on the annual  $\text{NH}_3$  concentration appeared to be a minor factor on a decadal scale at most of the sites, although it can be the dominant one at a few sites. For example, the strongest spike of atmospheric  $\text{NH}_3$  at NM98 occurred in July 2014, the year in which PDI exhibited a large negative deviation from the decadal average (Figure 8a,b), but no spike was observed in July 2015, the year in which PDI exhibited a large positive deviation from the decadal average.

A hypothesis is thereby proposed to explain the contradictory results of atmospheric  $\text{NH}_3$  related to droughts between the event and annual time scales. Extreme drought very likely restrains the release of  $\text{NH}_3$  from soil and vegetation to the atmosphere because the release is strongly driven by water evaporation.<sup>25,26</sup> However, extreme droughts may lead to the accumulation of  $\text{NH}_4^+$  in the surface soil layer because of the reduced loss by water runoff.  $\text{NH}_3$  can then be explosively released from the soil, as induced by occasional precipitation at time scales of minutes to hours, which consequently leads to a higher annual  $\text{NH}_3$  concentration.

Weather conditions are also expected to regulate the explosive release of  $\text{NH}_3$  from fertilizer applications because of the effects of the ambient temperature on water evaporation, the degradation rate of urine, etc. For example, at Saint-Anicet, Québec, large increases in atmospheric  $\text{NH}_3$  (e.g., with the daily average reaching approximately  $30 \mu\text{g m}^{-3}$ ) were observed in most years from 2006 to 2014, but not in the other years (Figure S1b). A value higher than  $80 \mu\text{g m}^{-3}$  was observed at the site on October 23, 2010, and another spike higher than  $10 \mu\text{g m}^{-3}$  was again observed on November 4,



**Figure 7.** Correlations of the annual averages of atmospheric  $\text{NH}_3$  at OH02 and OH27 with either ambient temperature (a) or PDI data (b).



**Figure 8.** Temporal variation in atmospheric  $\text{NH}_3$  at NM 98 (a), weekly variations in PDI in different years and decade average (b), and correlations between annual averages of atmospheric  $\text{NH}_3$  and PDI data at NM98 (c).

2010, corresponding to the fall fertilizing season in Canada. Such high values likely resulted from explosive releases of  $\text{NH}_3$  from fertilization applications. There were also many summer spikes at magnitudes of  $<10 \mu\text{g m}^{-3}$ , likely from the release of the residual spring fertilization.<sup>11</sup>

### 3. METHODOLOGY

Monitoring sites having at least 8 years of atmospheric  $\text{NH}_3$  data were selected in this study (Tables S1 and S2, Figure 1). Daily (one in every three days) mass concentrations of atmospheric  $\text{NH}_3$  at seven Canadian sites were downloaded from the National Air Pollution Surveillance (NAPS, <http://maps-cartes.ec.gc.ca/rnspa-naps/data.aspx?lang=en>) network, and biweekly mass concentrations of atmospheric  $\text{NH}_3$  at 15 sites in the United States were downloaded from the Passive Ammonia Monitoring Network (AMoN, <http://nadp.slh.wisc.edu/AMoN/>). Simultaneous measurements of  $\text{NH}_4^+$  mass concentrations in  $\text{PM}_{2.5}$  and meteorological data at the Canadian NAPS sites were also downloaded to facilitate the analysis. Concentrations of  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$  at IMPROVE sites and Environmental Protection Agency sites in the United States (<http://vista.cira.colostate.edu/Improve/>) were also used because of the lack of simultaneous measurements of  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$  at some of the AMoN sites. The weather data, including the PDI, ambient temperature, and precipitation, were downloaded as well ([http://www.cpc.ncep.noaa.gov/products/analysis\\_monitoring/cdus/palmer\\_drought/](http://www.cpc.ncep.noaa.gov/products/analysis_monitoring/cdus/palmer_drought/)).  $\text{NH}_3$  emission data at the provincial level in Canada were obtained from <https://pollution-waste.canada.ca/air-emission-inventory/>, and those at state level in the United States were

obtained from <https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data>.

The starting month and year for  $\text{NH}_3$  monitoring varied with each site (Tables S1 and S2). To obtain the longest time series for the annual average mass concentrations of atmospheric  $\text{NH}_3$ , a 1 year period was chosen from June to the following May at most Canadian NAPS sites and from September to the following August at most American sites, in lieu of using a calendar year. More details on the data can be obtained from the aforementioned websites and previous studies.<sup>16,17,39</sup> Information on the  $\text{NH}_4^+$  sampling sites in the United States is listed in Table S3.

Annual  $\text{NH}_3$  concentrations are used for generating trends. For any given site with a significant trend in atmospheric  $\text{NH}_3$ , the total percentage increase between the start and end year is calculated, taking the start year as the base. The percentage decrease in  $\text{NH}_3$  emissions in each province or state is calculated in the same way. The M–K analysis tool has been widely used for trend analysis and is also used in the present study. The method can resolve qualitative trends including “an increasing/decreasing trend with a  $P$  value of  $<0.05$ ”, “a probable increasing/decreasing trend with a  $P$  value of  $0.05$ – $0.1$ ”, “a stable trend with a  $P$  value of  $>0.1$  and a ratio of  $<1.0$  between the standard deviation and the mean of the data set”, and “no trend for all the other conditions”.<sup>16,40</sup> Using the Sen’s slope, it can yield a quantitative result. LR analysis was also conducted to support the M–K analysis results.

### ■ ASSOCIATED CONTENT

#### § Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.9b03284>.

Information of sampling sites of atmospheric  $\text{NH}_3$  and  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$  in Canada; information of sampling sites of atmospheric  $\text{NH}_3$  in the United States; information of sampling sites of  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$  in the United States; information of weather stations in the United States; biweekly averages of atmospheric  $\text{NH}_3$  measured at TX43 and daily averages of atmospheric  $\text{NH}_3$  measured at Saint-Anicet of Quebec; annual  $\text{NH}_3$  emissions from wildfire in various states in the United States; correlations of  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$  between two neighboring sites in the United States; adjusted annual averages of atmospheric  $\text{NH}_3$  at OH02, IN99, and SC05 in the United States using approach 1 and approach 2 (PDF)

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#### Notes

The authors declare no competing financial interest.

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